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One-Pot Synthesis of Xanthate-Functionalized Cellulose for the Detection of Micromolar Copper(II) and Nickel(II) Ions

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A one-pot synthesis and application of cellulose-based sensors to efficiently detect various toxic metal ions in aqueous solutions in micromolar quantities is reported. Cellulose microfibers have been functionalized with carbon disulfide in alkaline solution to form cellulose xanthate. The material detects several toxic metal ions such as copper, nickel, or cobalt ions through color change detectable by the naked eye. The optical sensor can be used as an ideal flash test for assessing the quality of drinking water.

1. Introduction

While the use of functionalized or modified cellulose for the removal of different pollutants such as dyes,[1] pharmaceuticals,[2] bacteria,[3] toxic metal ions,[4] or nanoparticles[5] from water has been looked at thoroughly in the past decades, only a few research groups dedicated their work to the use of functionalized cellulose as an optical sensor for various pollutants.[6] Cellulose-based sensors have previously been used in flexible electronics[7] and microfluidic devices.[8] Recently, sensors based on cellulose have been developed to detect nickel,[9] copper,[10] iron,[11] and cyanide[12] ions. A universal detector for copper, nickel, cobalt, and zinc, based on 2-carboxy-2′-hydroxy-5′-sulfoformazyl benzene (zincon), has been described.[13] Toxic metals are, for example, used for plumbing,[14] electroplating,[15] and catalysis.[16] The various usages may lead to pollution, if the wastewater is not disposed of or treated properly, which can cause serious diseases like infantile liver cirrhosis.[14] Therefore, both reliable and affordable methods are needed to analyze the quality of wastewater before it enters the environment and potable water supply.

The viscose method is one of the few known ways for dissolving the biopolymer cellulose, which is achieved in the presence of sodium hydroxide in carbon disulfide. It has been discovered at the end of the 19th century and has been used for spinning the viscose rayon fiber, which in turn can be used for the fabrication of clothing. Under acidic conditions, the dissolved cellulose precipitates.[17] A degree of functionalization of hydroxyl groups to xanthate groups of 20% to 35% is reported.[18]

Instead of pursuing sophisticated and thus chemically expensive and hardly feasible routes for functionalization of cellulose, we chose to go back to the roots and look at the performance of the well-explored viscose method. Using this method, the cellulose backbone is decorated with xanthate groups ($-CS_2^-$), which interact with various metal ions in the aqueous solution to form colored complexes that are visible by the "naked eye" and can be analyzed with UV–vis spectroscopy. The sensor presented herein is universally usable for various toxic metal ions in the micromolar range including copper, nickel, lead, and cobalt. In the case of copper, it possesses the lowest limit of detection (LOD) compared to other metal-free cellulose-based colorimetric ion sensors. The sensor can be synthesized in a one-pot reaction using inexpensive reactants and preserves its ability to sense metal ions even over multiple months if kept under the exclusion of air and water.

2. Experimental Section

Cellulose fibers (2 g) were suspended in aqueous KOH (30 mL, 5 wt%). Carbon disulfide (10 mL) was added to the mixture and stirred for 3 h. The color of the mixture changed to deep orange with a significant increase in viscosity of the solution. Deionized water (50 mL) was added to the viscose solution in order to precipitate the functionalized cellulose, which was separated by vacuum filtration. The functionalized cellulose was washed with water and ethanol until the filtrate became neutral. The final product was dried in a desiccator in vacuo.

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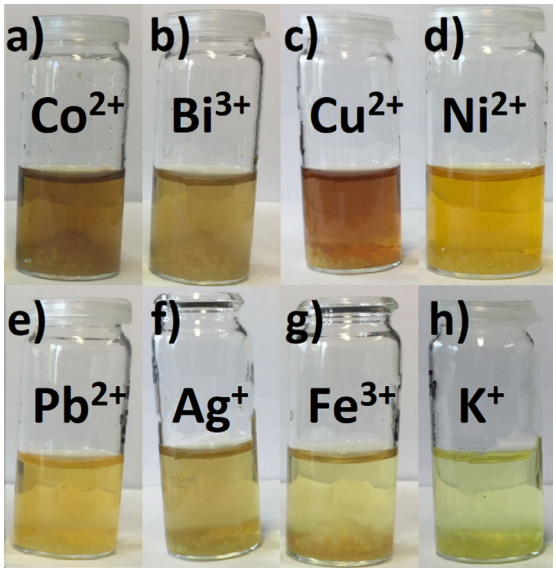

Figure 1. Color change observed when 50 mg of the functionalized cellulose are put in contact with the respective toxic metal ion solutions (10 mg L^{-1}) and potassium ion solution (100 mg L^{-1}). The color observed for K^{+} is equal to the color observed when the functionalized cellulose is being brought in contact with pure deionized water.

Color change experiments were carried out using 50 mg of the as-synthesized cellulose. The prepared metal ion solutions in the range from 0 and 100 mg L^{-1} were poured over the cellulose. For the nickel(II) nitrate and the copper(II) sulfate solutions, the colored supernatant was analyzed via UV–vis spectroscopy (Thermo Fischer Scientific Evolution 220 UV–visible spectrophotometer). A list of all used chemicals including suppliers and purities is provided in Table S1, Supporting Information.

3. Results and Discussion

Chemical functionalization of cellulose occurs via the hydroxyl (–OH) groups on the backbone. Various functional groups have been connected to cellulose mainly via esterification.[19] The pathway that was chosen for this study is deprotonation of the hydroxyl groups in strongly alkaline conditions, followed by nucleophilic attack on carbon disulfide to form cellulose xanthate (Scheme S1, Supporting Information). Scanning electron microscopy images of cellulose xanthate show a typical fibrous structure, indicating that the structure is maintained during functionalization (Figure S1, Supporting Information). A degree of functionalization of 4% in sulfur has been determined via elemental analysis (Table S2, Supporting Information).

In a preliminary series of experiments, the functionalized cellulose was exposed to several metal ion solutions to observe complex formation through change in color (**Figure 1**). As shown in Scheme S1, Supporting Information, two mechanisms that explain the color change are currently hypothesized: a) each xanthate group is binding to a metal ion, and b) a chelate complex is formed, where two xanthate groups are binding to a doubly charged metal ion. The change of color is the most evident for copper(II), nickel(II), cobalt(II), and lead(II) ions, but can, nevertheless, also be determined by the "naked eye" for bismuth(III), silver(I), and iron(III) ions. However, for the latter four metal ions, the color quickly returned to the natural color of the solution. A blind test with potassium ions showed no significant color change in solution. A list of all tested metal ions and occurring color changes is shown in Table S3, Supporting Information. Stored in a dry vacuum sealed container, the sensor maintains its ability to detect metal ions in low concentrations for multiple months.

The changes in color with respect to the concentration of the metal ion have been determined for copper(II) and nickel(II) solutions (**Figure 2**). For both ions, the increasing intensity of the

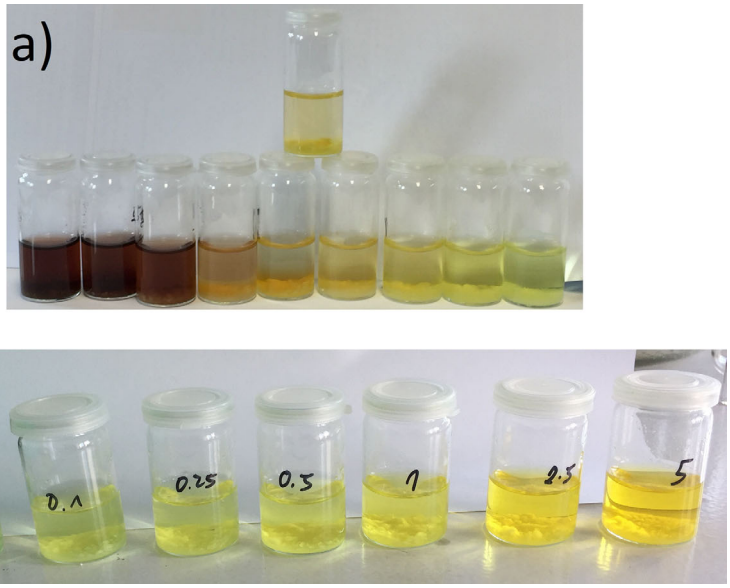

Figure 2. a) Concentration series of Cu^{2+} (in contact with the sensor), from left to right: 100, 50, 25, 10, 5, 2.5, 1, 0.5, and 0 mg L^{-1}. The sample on top of the others is obtained from tap water from the Department of Chemistry of the Humboldt University of Berlin that was put in contact with functionalized cellulose. b) Concentration series of Ni^{2+} (in contact with the sensor) from left to right: 0, 0.1, 0.25, 0.5, 1, 2.5, and 5 mg L^{-1}.

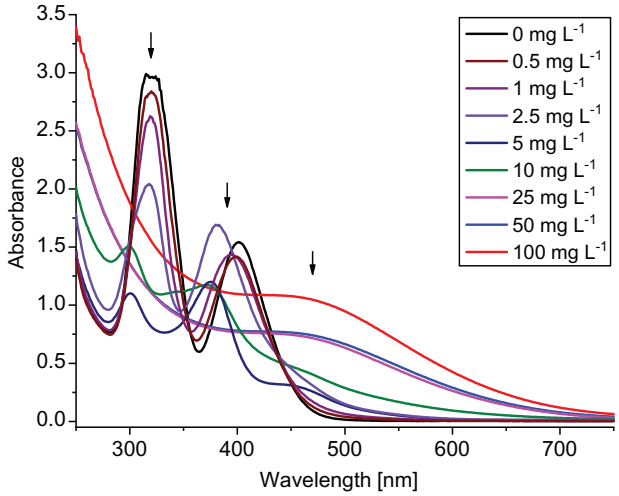

Figure 3. UV–vis absorption spectra of the supernatant solutions of different concentrations of Cu^{2+} ions in contact with the functionalized cellulose. The observed absorption bands are labeled.

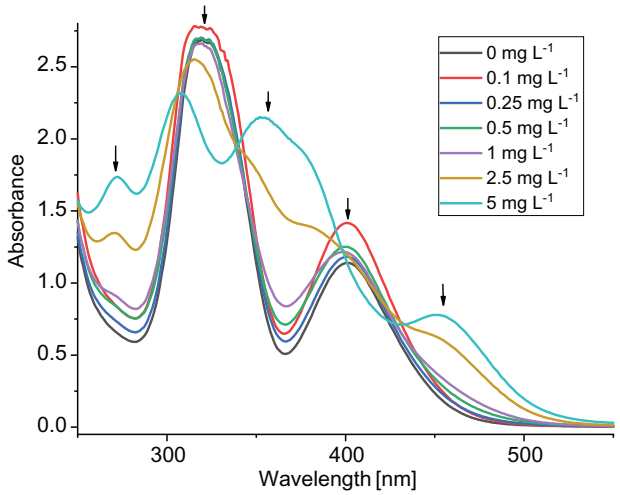

Figure 4. UV–vis absorption spectra of the supernatant solutions of different concentrations of Ni^{2+} ions in contact with the functionalized cellulose. The observed absorption bands are labeled.

color can be detected by the "naked eye" even for low concentrations. The solutions obtained can thus be used as a reference for determining the concentration of unknown solutions. To prove the ability of the functionalized cellulose to detect toxic metal ions in real samples, tap water from the Department of Chemistry of the Humboldt University of Berlin was brought in contact with the developed sensor. The observed color intensity was compared to the samples with fixed concentrations (Figure 2a). A concentration between 2.5 and 5 mg L^{-1} can clearly be identified, which is in agreement with atomic absorption spectroscopy studies of the tap water that showed a Cu(II) concentration of 3.5 mg L^{-1}. The measured concentration of Cu(II) ions in the tap water is above the maximum permissible value of 2 mg L^{-1} according to the WHO.[20]

UV–vis spectra of the supernatant Cu(II) ion solutions shown in Figure 2a have been recorded (**Figure 3**). Three notable absorption bands at 320, 400, and 460 nm were observed. The bands at 320 and 400 nm are distinctive for low concentrations and decrease with an increasing concentration of copper ions. The band at 320 nm shifts to lower wavelengths upon increasing concentrations before disappearing completely. An intense band at 460 nm arises for increasing concentrations of copper above 10 mg L^{-1}. The absorbance of the UV–vis bands at 320 and 460 nm shows a linear behavior if plotted against the concentration for either low (320 nm) or high (460 nm) concentrations of metal ions (Figure S2, Supporting Information). The LOD with this method is 0.076 ± 0.003 mg L^{-1} (1.20 ± 0.05 µM) while the limit of quantification (LOQ) is 0.25 ± 0.01 mg L^{-1} (3.9 ± 0.2 µM).

Similar UV–vis spectra have been recorded for the Ni(II) ion solutions (**Figure 4**). Generally, the absorption band at 320 nm decreases with increasing concentrations of Ni(II) ions, while its maximum shifts to lower wavelengths. Another band at 400 nm shows no linear behavior upon increasing Ni(II) ion concentrations, while the absorption bands at 280, 355, and 455 nm only start to appear at higher concentrations. Again, the absorbance at 320 nm can be plotted against the concentration and shows a linear behavior (Figure S3, Supporting Information). For Ni(II), an LOD of 0.23 ± 0.04 mg L^{-1} (3.9 ± 0.7 µM) and an LOQ of 0.8 ± 0.1 mg L^{-1} (13 ± 2 µM) have been calculated.

The LOD of the colorimetric sensor presented herein has been compared to those of other optical sensors for Ni(II) and Cu(II) ions (**Table 1**). For Cu(II), cellulose xanthate performs better than comparable cellulose-based detectors, while other detectors relying on fluorescence or using potential toxic metal nanoparticles perform slightly better.[10,21] For Ni(II), cellulose xanthate performs not as good as the sensors presented in literature.[22]

Table 1. LOD of cellulose xanthate compared to colorimetric metal ion detectors reported in the literature.

Functionalization	Ion	LOD [µM]	Reference
Cellulose xanthate	Cu^{2+}	1.2	
Cellulose/thioglycolic acid	Cu^{2+}	33	[10a]
Cellulose/Ti_6O_{11},TPED,Cupron	Cu^{2+}	<0.1	[21a]
Protein-nanocellulose	Cu^{2+}	0.2[a)]	[10b]
Cellulose/1,4-dihydroxyanthraquinone	Cu^{2+}	<0.1[a)]	[21b]
Dual-DNAzyme	Cu^{2+}	1	[21c]
Protein functionalized gold nanoparticles	Cu^{2+}	0.2	[21d]
Silver/dopamine nanoparticles	Cu^{2+}	0.1	[21e]
Cellulose xanthate	Ni^{2+}	4	
Cellulose paper with zincon/HNS	Ni^{2+}	<0.1	[9]
Triacetyl cellulose/triazene-1-oxide	Ni^{2+}	<0.1	[22a]
Acetyl cellulose/dithiocarboxylic acid	Ni^{2+}	0.5	[22b]
Quinoline based sensor	Ni^{2+}	0.2	[22c]
Amino acid functionalized silver nanoplates	Ni^{2+}	0.1	[22d]

[a)]These cellulose-based sensors detect metal ions via fluorescence, not via color change.

4. Conclusion

A cellulose based sensor for various toxic metal ions in the micromolar range has been developed and its feasibility as a naked eye colorimetric detector has been proven with both artificially prepared and real samples. The modified cellulose possesses excellent potential for being used as a rapid detector for contamination of water with various toxic metal ions. For Cu(II), the maximum permissible value of 2 mg L^{-1} is exactly within the detectable range of the cellulose xanthate sensor. Due to the sensor's ability to reliably detect various metal ions, its ease of application, and its estimated low cost of production, the sensor can be considered as the perfect flash test for assessing the quality of potable water in rural areas or third world countries. The incorporation of the sensor on a lab-on-a-chip device and its longevity will be subject of future studies.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

cellulose, cellulose xanthate, colorimetric sensors, metal ion detection, viscose processes

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